

104-01-00

[Name of the Document] Specification

[Title of the Invention] Method for Manufacturing  
Electron-emitting Device and Image Forming Apparatus Using  
Near Infrared Ray Absorbing Organic Metal Substance

[What is Claimed is:]

[Claim 1] A method for manufacturing an electron-emitting device comprising forming a thin film including an electron-emitting material between oppositely arranged device electrodes, baking the thin film and then electrically energizing the thin film to form an electron-emitting region, characterized in that a near infrared ray absorbing organic metal substance is used in the thin film.

[Claim 2] The method for manufacturing an electron-emitting device according to Claim 1, wherein said near infrared ray absorbing organic metal substance is an organic metal compound having a near infrared ray absorbing group introduced.

[Claim 3] The method for manufacturing an electron-emitting device according to Claim 1, wherein said near infrared ray absorbing organic metal substance is a composition comprising an organic metal compound and a near infrared ray absorbing material.

104-01-00

[Claim 4] The method for manufacturing an electron-emitting device according to Claim 1, wherein said baking is carried out by irradiating near infrared rays.

[Claim 5] The method for manufacturing an electron-emitting device according to Claim 1, wherein a near infrared ray absorbing organic metal substance is applied to a substrate having device electrodes formed thereon to form a thin film, only the portion of the thin film which is intended to form an electron-emitting region is baked by irradiating near infrared rays, and the near infrared ray absorbing organic metal substance remaining in the thin film other than the portion which is intended to form an electron-emitting region, is removed with a solvent.

[Claim 6] A method for manufacturing an image forming apparatus having a plurality of electron-emitting devices, each of the electron-emitting devices being manufactured by forming a thin film including an electron-emitting material between oppositely arranged device electrodes, baking the thin film, and then electrically energizing the thin film to form an electron-emitting region, characterized in that a near infrared ray absorbing organic metal substance is used in the thin film.

104-01-00

[Detailed Description of the Invention]

[0001]

[Field of the Industrial Utilization]

The present invention relates to a method for manufacturing an electron-emitting device and an image forming apparatus.

[0002]

[Prior Art]

There have been known two types of electron-emitting device; the thermoelectron type and the cold cathode type. The cold cathode type included the field emission type (abbreviated as FE hereinafter), the metal/insulation layer/metal type (abbreviated as MIM hereinafter) and the surface conduction electron-emitting device (abbreviated as SCE hereinafter).

[0003]

Examples of FE have been disclosed in W.P. Dyke & W.W. Dolan, "Field emission", Advance in Electron Physics, 8, 89 (1956) and C.A. Spindt, "Physical properties of thin film-field emission cathodes with molybdenum cones", J. Appl. Phys., 47, 5248 (1976).

[0004]

An example of MIM has been described in C.A. Mead, "The Tunnel-emission amplifier", J. Appl. Phys., 32, 646 (1961).

[0005]

104-01-00

An example of SCE has been described in M.I. Elison,  
Radio Eng. Electron Phys., 10 (1965).

[0006]

As the surface conduction electron-emitting device (SCE), there have been reported one using a  $\text{SnO}_2$  thin film by M.I. Elison mentioned above; one using an Au thin film [G. Dittmer, "Thin Solid Films", 9, 317 (1972)], one using an  $\text{In}_2\text{O}_3/\text{SnO}_2$  thin film [M. Hartwell and C.G. Fonstand, "IEEE Trans. ED Conf." 519 (1975)] and one using a carbon thin film [Araki et al., Vacuum, No. 1, 22 (1983)].

[0007]

Fig. 10 is an example of a typical constitution of a surface conduction electron-emitting device. A thin film for forming an electron-emitting region is formed, for example, as follows. A tape or resist film is provided at the portion of a thin film in which a thin film for forming an electron-emitting region is not desired to be formed, an organic metal compound is applied to the thin film by dipping or spinner coating, a fine particle film is formed at the given portion by removing the tape or resist film, and the thin film is baked at several hundreds °C to form an thin film 2 for forming an electron-emitting region comprising metal or metal oxide fine particles.

[0008]

In the surface conduction electron-emitting device,

104-01-00

a thin film 2 for forming an electron-emitting region is generally subjected to an electrically energizing treatment called electric forming to form an electron-emitting region 3 before conducting electron emission. The electric forming is carried out by applying a voltage to both ends of the thin film 2 for forming an electron-emitting region, by which the thin film 2 causes to locally destroy, deform or modified to form the electron-emitting region 3 having an electrically high resistance. The electron-emitting region 3 has cracks generated at the given position of the thin film 2, and electrons are emitted from near the cracks. Hereinafter, the thin film 2 for forming an electron-emitting region including an electron-emitting region formed by electric forming refers to a thin film 4 including an electron-emitting region.

[0009]

[Problems to be solved by the Invention]

However, a method for manufacturing a thin film for forming an electron-emitting region comprising forming a thin film composed of an organic metal compound mentioned above and baking the thin film includes the following problems.

[0010]

(1) A thin film for forming an electron-emitting region is required to form on only a part of a substrate

# 104-01-001

and device electrodes. The conventional method requires to form a thin film comprising an organic metal compound on the entire surface of the substrate and the device electrode and remove the unnecessary part of the thin film. Therefore, the expensive organic metal compound is not sufficiently utilized.

(2) A photolithography process using a photoresist needs to use in the step of removing the unnecessary part mentioned above, thereby the process becomes complex and production cost increases.

(3) Since all the materials including the substrate and the device electrodes are simultaneously heated to from 300°C to 400°C in the baking step, these materials needs to have a high heat resistance.

[0011]

An object of the present invention is to provide a method for manufacturing an electron-emitting device and an image forming apparatus in which a near infrared absorbing property is imparted to a thin film comprising an organic metal compound, and utilization efficiency of the organic metal compound is increased by selectively heating only the portion of the thin film which is intended to form an electron-emitting region with laser beams, and an electrode material is not to subjected to an excessive thermal load without using a photolithography process.

104-01-00

[0012]

[Means for Solving the Problems]

The present invention provides a method for manufacturing an electron-emitting device comprising forming a thin film including an electron-emitting material between oppositely arranged device electrodes, baking the thin film and then electrically energizing the thin film to form an electron-emitting region, characterized in that a near infrared ray absorbing organic metal substance is used in the thin film.

[0013]

The present invention further provides a method for manufacturing an image forming apparatus having a plurality of electron-emitting devices, each of the electron-emitting devices being manufactured by forming a thin film including an electron-emitting material between oppositely arranged device electrodes, baking the thin film, and then electrically energizing the thin film to form an electron-emitting region, characterized in that a near infrared ray absorbing organic metal substance is used in the thin film.

Fig. 1 is process steps illustrating one embodiment of a method for manufacturing an electron-emitting device according to the present invention. Fig. 2 is a drawing illustrating one example of an electron-emitting device manufactured by the method of the present invention.

1104-01-00

Fig. 2(a) is a plane view of the electron-emitting device and Fig. 2(b) is a cross-sectional view taken along a line A-A in Fig. 2(a).

[0014]

A method for manufacturing an electron-emitting device according to the present invention will be described below by referring to Figs. 1 and 2.

(1) After thoroughly cleaning an insulating substrate 1 with a detergent, pure water and an organic solvent, a device electrode material are laminated on the insulating substrate by vacuum vapor deposition or sputtering, and device electrodes 5 and 6 are formed on the surface of the insulating substrate 1 using a photo-lithography technique.

(2) Next, a solution of a near infrared ray absorbing organic metal substance is rotationally applied to the entire surface of the insulating substrate including the device electrodes and allowed to stand to form a thin film 8 comprising the near infrared ray absorbing organic metal composition.

[0015]

(3) Thereafter, the portion R inside the dotted line in Fig. 4 is irradiated with a semiconductor laser, and only this portion is baked to form a metal or metal oxide fine particle thin film 10. The near infrared ray absorbing organic metal composition can be heated to from

104-01-00

300°C to 600°C usually by irradiating a semiconductor laser having a wavelength of 830 nm, an output of from 5 to 30 mW, a pulse width of from 1 to 10  $\mu$ sec, and a beam diameter of from 1 to 3  $\mu$ m. However, the heating temperature and the baking temperature are different depending on the characteristics of the near infrared ray absorbing organic metal composition, the substrate and the device electrodes, and the optimum conditions are selected by changing the laser output, the pulse width and the pulse number.

[0016]

The entire region inside the dotted line in Fig. 4 can be baked by repeating movement of the substrate and irradiation with the laser. Thereafter, the near infrared ray absorbing organic metal composition in the unbaked portion is removed using an organic solvent to recover, thereby forming a thin film 2 for forming an electron-emitting region. The recovered near infrared ray absorbing organic metal composition is properly purified and can be reused.

[0017]

(4) Subsequently, the thin film 2 for forming an electron-emitting region is subjected to an electrically energizing treatment called electric forming by applying a voltage in a pulse form or a high speed increasing voltage between device electrodes 5 and 6 from a power

104-01-00

source (not shown), thereby an electron-emitting region 3 having a changed structure is formed at a given portion of the thin film 2 for forming an electron-emitting region. The portion of the thin film 2 for forming an electron-emitting region having a changed structure locally destroyed, deformed or modified by the electrically energizing refers to the electron-emitting region 3.

[0018]

Fig. 6 shows a voltage wave form used in the electric forming.

In Fig. 6,  $T_1$  and  $T_2$  are the pulse width and the pulse interval of the voltage wave form, and in this example,  $T_1$  was from 1 microsecond to 10 milliseconds and  $T_2$  was from 10 microseconds to 100 milliseconds and the wave height of the triangular wave (the peak voltage in the electric forming) was from 4 V to 10 V, and the electric forming was carried out under a vacuum atmosphere for about several tens seconds.

[0019]

When the electron-emitting region is formed mentioned above, a triangular pulse voltage is applied to the device electrodes in an electric forming, but the pulse voltage may have a different waveform such as a rectangular waveform. The wave height, the pulse width and the pulse interval are not limited to the above values

104-01-00

and the proper values may be selected if the good electron-emitting region is formed.

[0020]

The characteristics of the electron-emitting device of the present invention manufactured by the method mentioned above are measured using a gauging system in Fig. 5.

Fig. 5 is a schematic block diagram of a gauging system for determining the electron-emitting performance of the electron-emitting device having a constitution shown in Fig. 2. In Fig. 5, reference numeral 1 shows an insulating substrate, 5 and 6 show device electrodes, 4 shows a thin film including an electron-emitting region, and 3 shows an electron-emitting region. The gauging system comprises a power source 31 for applying a device voltage  $V_f$  to the device, an ammeter 30 for measuring the device current  $I_f$  running through the thin film 4 including an electron-emitting region between the device electrodes 5 and 6, an anode 34 for capturing the emission current  $I_e$  emitted from the electron-emitting region of the device, a high voltage source 33 for applying a voltage to the anode 34, and an ammeter 32 for measuring the emission current  $I_e$  emitted from the electron-emitting region 3 of the device.

[0021]

For measuring the device current  $I_f$  and the emission

1104-01-00

current  $I_e$  of the electron-emitting device, the power source 31 and the ammeter 32 are connected to the device electrodes 5 and 6, and the anode 34 connected to the power source 33 and the ammeter 32 is arranged above the electron-emitting device. The electron-emitting device and the anode 34 are provided in a vacuum chamber which is equipped with necessary instruments such as an exhaust pump and a vacuum gauge, thereby the gauging operation can be conducted under a desired vacuum condition. The gauging operation is conducted in a range of from 1 to 10 kV of voltage to the anode and from 3 to 8 mm of distance  $H$  between the anode and the electron-emitting device.

[0022]

Fig. 7 shows a typical example of relationships between the emission current  $I_e$  and the device current  $I_f$  and the device voltage  $V_f$  measured by the gauging system shown in Fig. 5. In Fig. 7, the emission current  $I_e$  and the device current  $I_f$  are shown in an arbitrary unit, because the values of  $I_f$  and  $I_e$  are significantly different.

[0023]

In the present invention, the near infrared ray absorbing organic metal substance can be prepared mainly by two methods: one is a method in which a near infrared absorbing property is imparted by introducing a near infrared ray absorbing group in an organic metal

# 1104-01-00

compound itself, and other is a method in which an organic metal compound and a near infrared ray absorbing compound are mixed to form a near infrared ray absorbing composition.

[0024]

Near infrared ray absorbing organic metal compounds that belong to the former category include, as illustrated in Chemical Formulas 1 through 11 below, phthalocyanine type metal complexes (1c, 1e, 1f, 2a and 2c), dithiol type metal complexes (3 through 6), mercaptonaphthol type metal complexes (7), polymethine type metal complexes (complexes of 37 with 8 through 22), naphthoquinone metal complexes (complexes of 37 with 26 through 28), anthraquinone type metal complexes (complexes of 37 with 29 through 34), triphenylmethane type metal complexes (complexes of 37 with 35 and 36) and aminium diimmonium type metal complexes (complexes of 37 with 23 through 25).

[0025]

Each near infrared ray absorbing organic metal composition belonging to the latter category is prepared by mixing an organic metal compound or an organic metal complex compound and a near infrared ray absorbing coloring matter. Near infrared ray absorbing coloring matters include phthalocyanine type coloring matters (1a, 1b, 1d and 2b), polymethine type coloring

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matters (8 through 22), naphthoquinone type coloring  
matters (26 through 28), anthraquinone type coloring  
matters (29 through 34), triphenylmethane type coloring  
matters (35 and 36) and aminium diimmonium type coloring  
matters (23 through 25).

[0025]

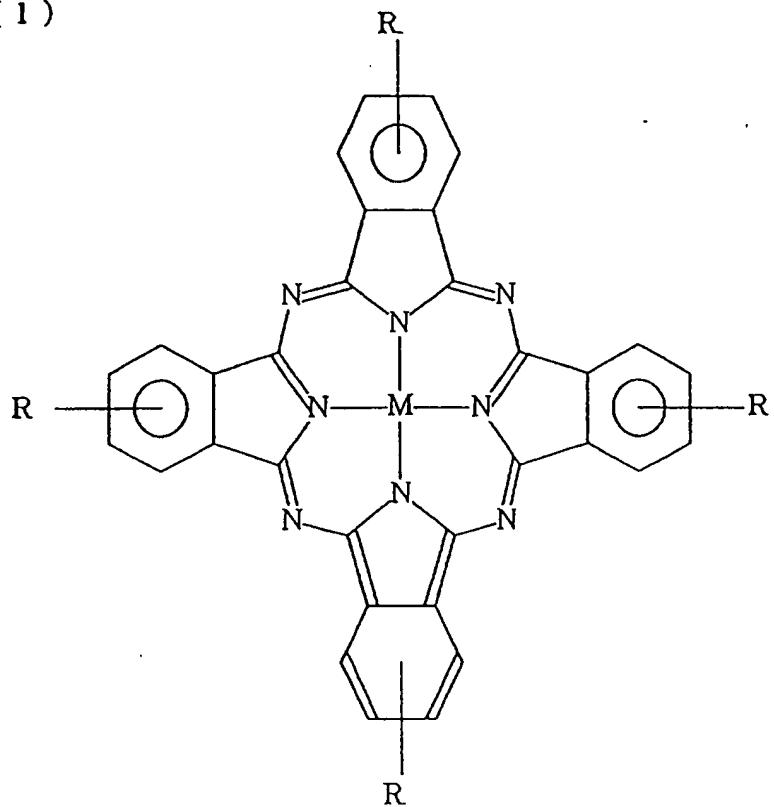
Organic metal compounds that can be used for this mode include those having one or more than one metal-carbon bonds, metal salts of organic acids, metal alkoxydes and organic metal complex compounds that can produce a metal or metal oxide if baked regardless of the metal contained in each compound. Example of compounds include metal salts of acetic acids (37) and acetylacetone metal complexes. The mol ratio of an organic metal compound and a near infrared ray absorbing coloring matter that can be used for this mode is found between 20:1 to 1:2 and preferably between 20:1 to 5:5. If the near infrared ray absorbing coloring matter falls under the lower limit, the resultant composition does not satisfactorily absorb near infrared rays whereas, if it exceeds the upper limit, a disproportionately large amount of near infrared rays is required for the baking operation.

[0027]

[Chemical Formula 1]

M(OH)<sub>0.1</sub>·HO

(1)



M = 2H      R = H                      1a

M = 2H      R = C(CH<sub>3</sub>)<sub>3</sub>              1b

M = Cu      R = F                      1c

M = 2H      R = -S-C<sub>6</sub>H<sub>4</sub>-CH<sub>3</sub>      1d

M = Ti      R = H                      1e

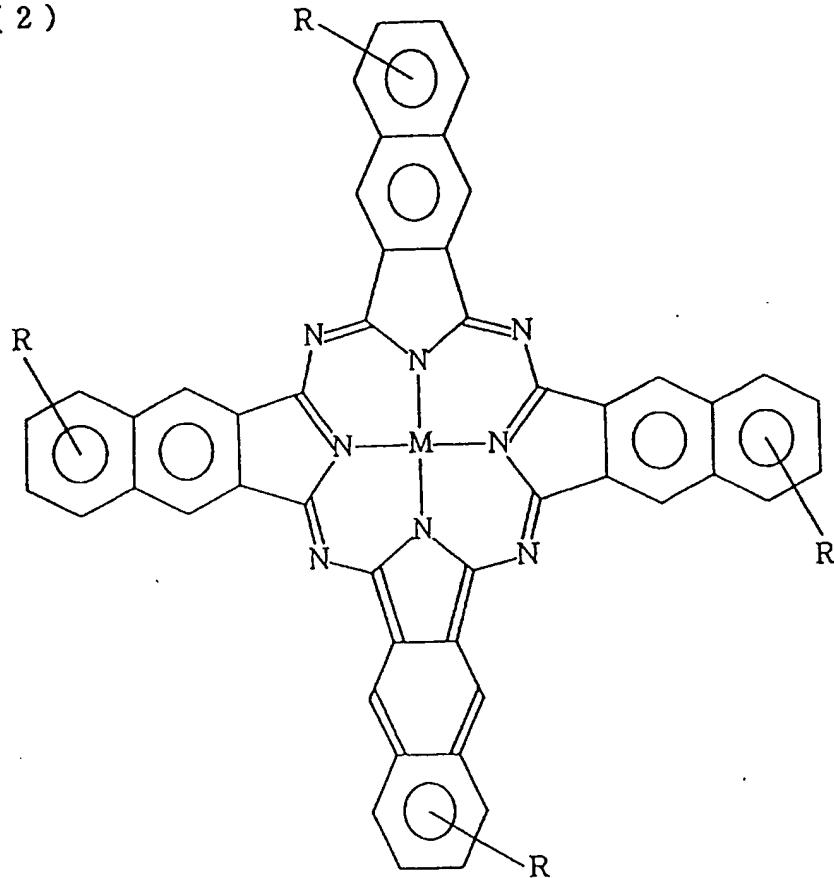
M = Pb      R = H                      1f

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[0028]

[Chemical Formula 2]

( 2 )



$M = Zn$        $R = H$       2a

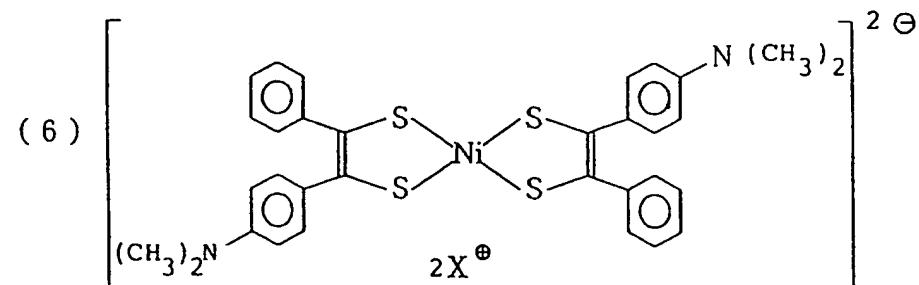
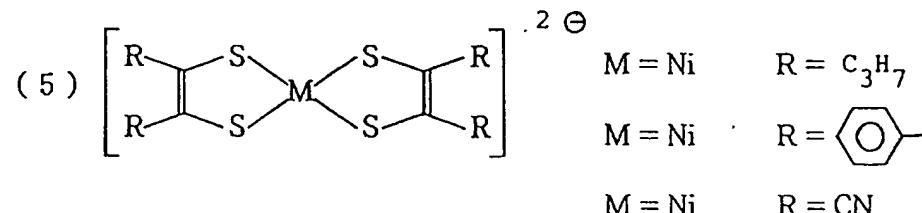
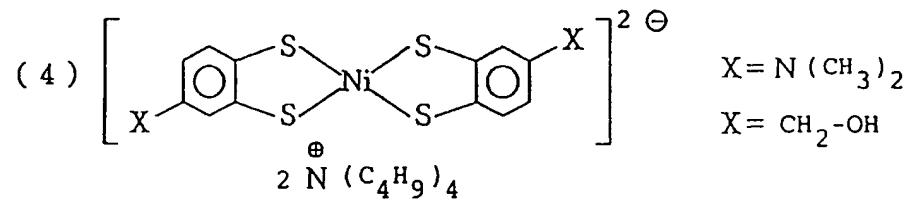
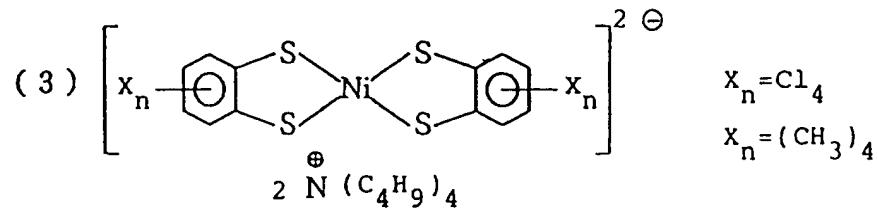
$M = 2H$        $R = F$       2b

$M = V$        $R = t - C_5H_{11}$       2c

1104-01-00

[0029]

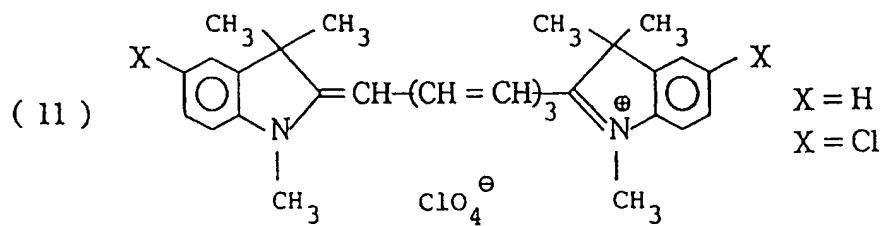
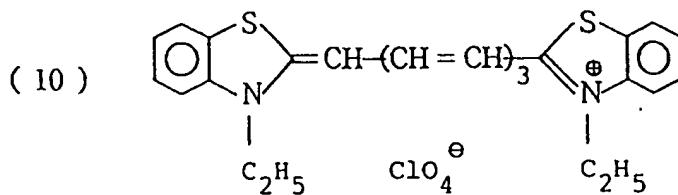
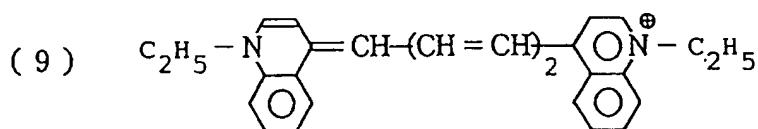
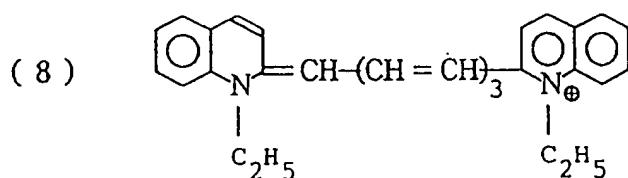
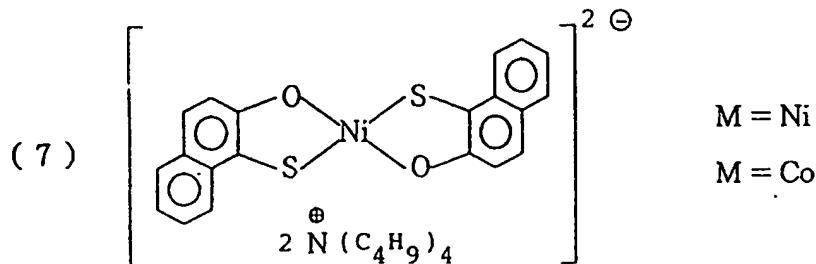
[Chemical Formula 3]



1104-01-00

[0030]

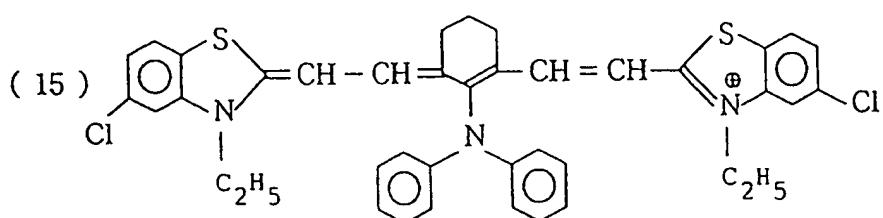
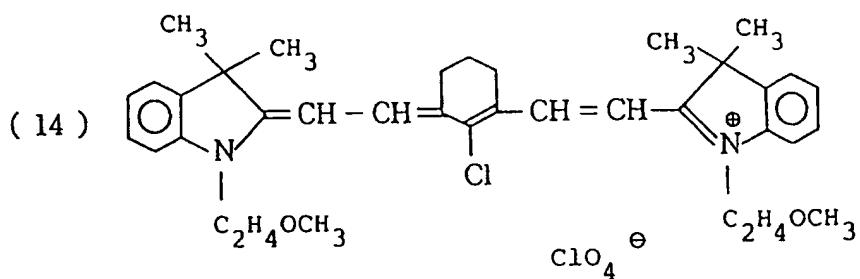
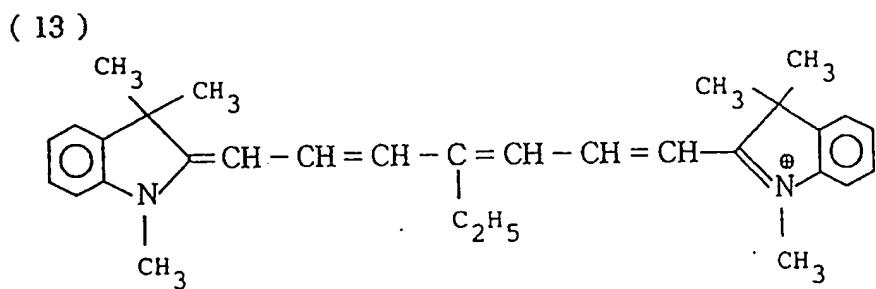
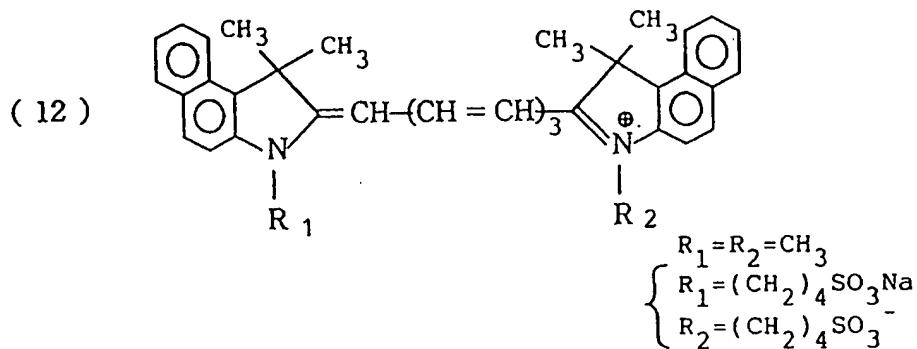
[Chemical Formula 4]



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[0031]

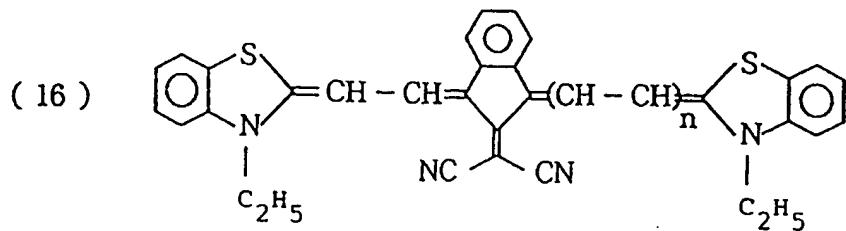
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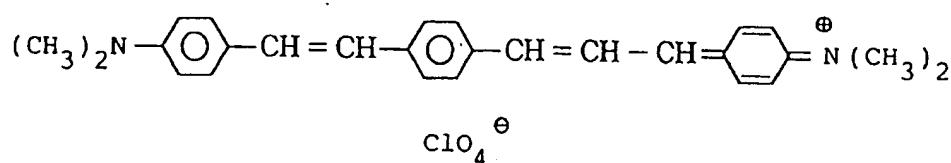
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[0032]

[Chemical Formula 6]



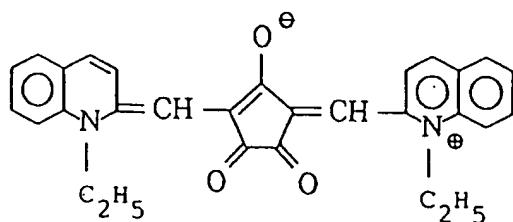
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(18)



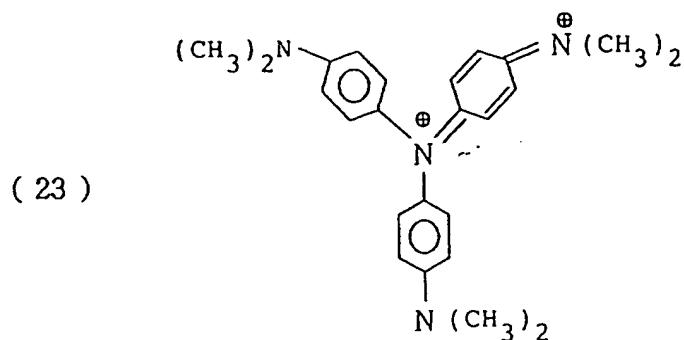
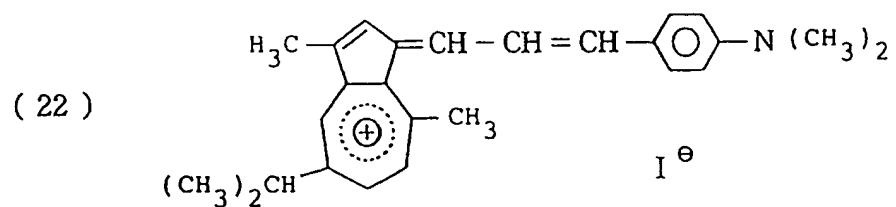
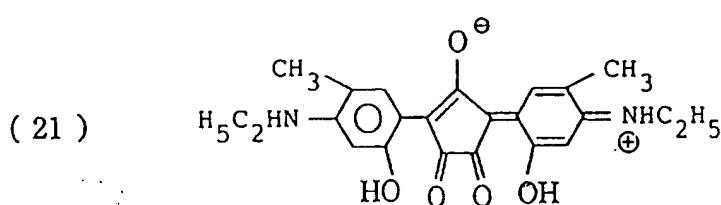
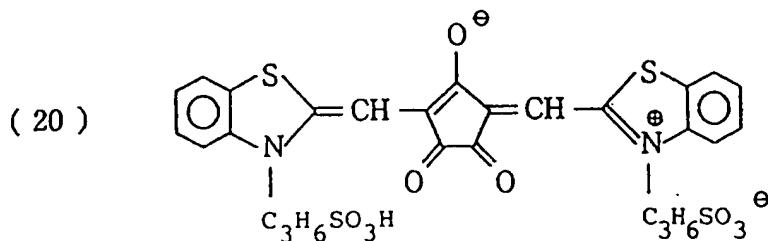
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[0033]

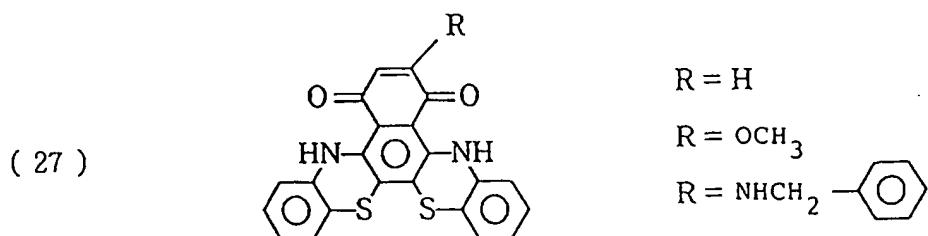
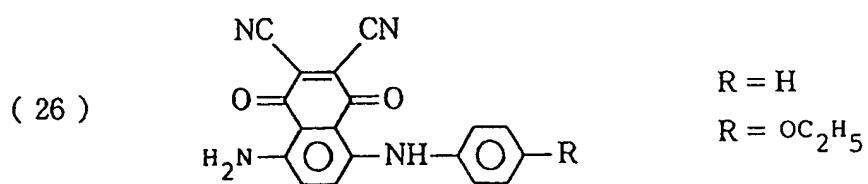
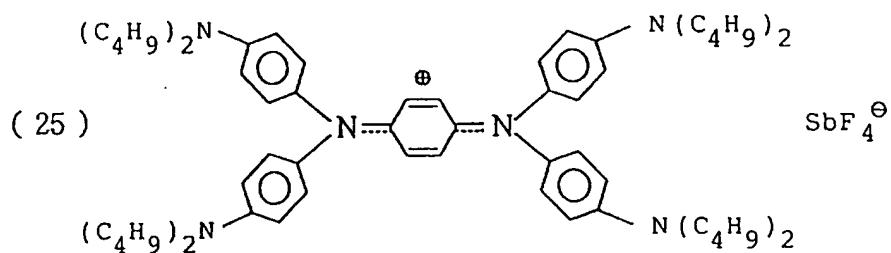
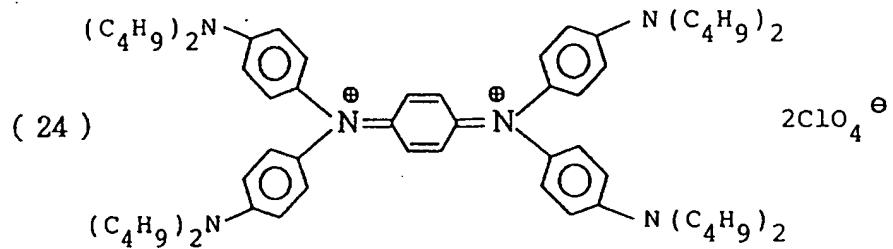
[Chemical Formula 7]



104-01-00

[0034]

[Chemical Formula 8]

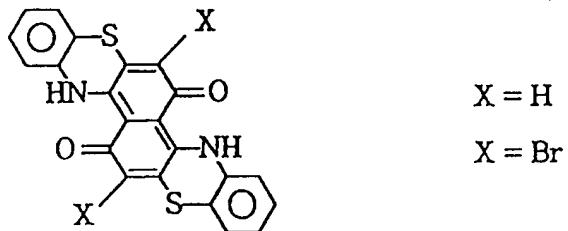


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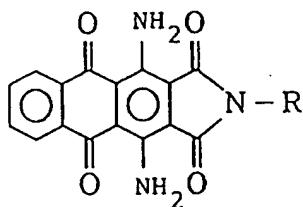
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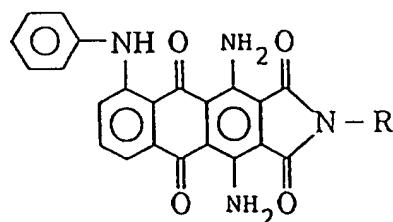
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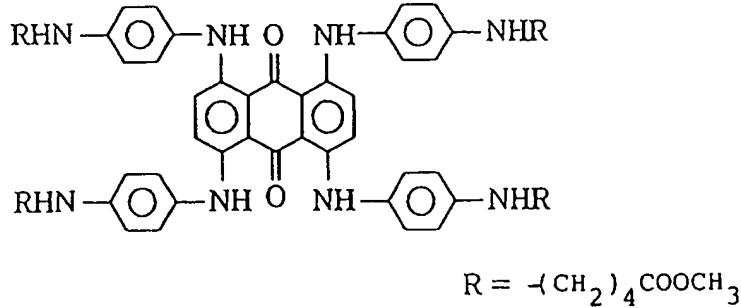
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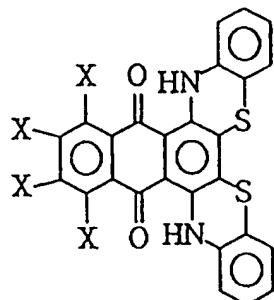


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[0036]

[Chemical Formula 10]

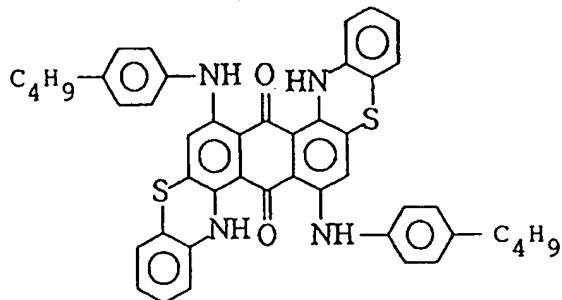
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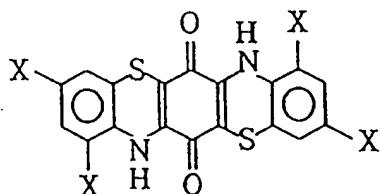
X = H

X = F

( 33 )



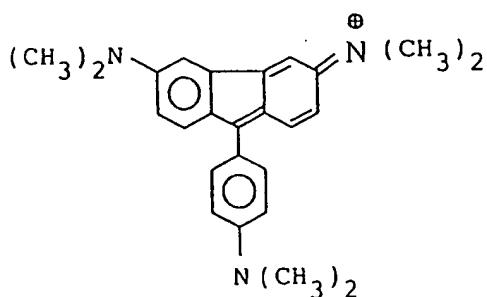
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X = Cl

X = CH3

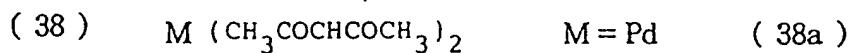
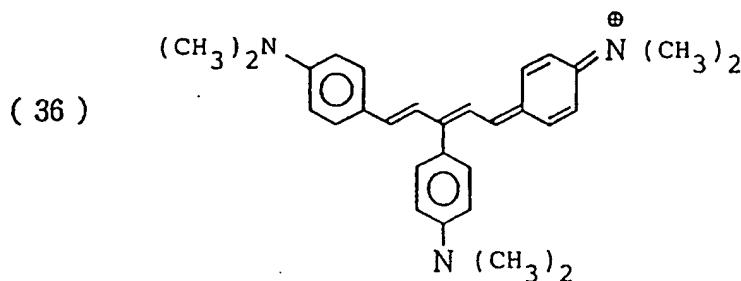
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# M OH · O · OO

[0037]

[Chemical Formula 11]



[0038]

A method for manufacturing an image forming apparatus such as a display apparatus according to the method of the present invention will be described below by referring to Fig. 8.

A plurality of electron-emitting devices 104 connected to X-directional wirings 105 and Y-directional wirings 106 which were not subjected to the electric forming were obtained by the steps of (a) through (e) in

1104-01-00

Fig. 1. After an electron source substrate having the plurality of electron-emitting devices 104 arranged on a substrate 101 was fixed on a rear plate 102, a face plate 110 (comprising a fluorescent film 108 and a metal back 109 formed on the inner surface of a glass substrate 107) was arranged at the position of 5 mm above the substrate 101 via a support frame 103. A frit glass was applied to the joint parts of the face plate 110, the support frame 103 and the rear plate 102 and baked at from 400°C to 500°C for 10 minutes or more in the atmosphere or a nitrogen atmosphere to hermetically seal (see Fig. 8).

[0039]

The rear plate 102 was also fixed to the substrate 101 with a frit glass. In Fig. 8, reference numeral 104 is the electron-emitting devices, and 105 and 106 are X-directional wirings and Y-directional wirings, respectively. In this embodiment, a enclosure 111 was constituted from the face plate 110, the support frame 103 and the rear plate 102. However, additional rear plate 102 is unnecessary when the substrate 101 itself has a sufficient strength because the rear plate 102 is provided in order to reinforce the strength of the substrate 101. In such a case, the support frame 103 is sealed directly to the substrate 101, and the enclosure 111 may be constituted from the face plate 110, the

3104-01-00

support frame 103 and the substrate 101.

[0040]

The fluorescent film 108 is made exclusively from a fluorescent substance if the apparatus is for displaying images in black and white, whereas it is made from fluorescent substances 113 and a black conductive material 112 which may be referred to as black stripes (Fig. 9(a)) or black matrix (Fig. 9(b)) depending on the arrangement of fluorescent substances 113 if the apparatus is for displaying color images. Black stripes or a black matrix are arranged for a color display panel so that the blurring of the fluorescent substances 113 of three different primary colors is made less recognizable and the adverse effect of reducing the contrast of displayed images of external light on the fluorescent film 108 is weakened by blackening the surrounding areas. In this embodiment, fluorescent substances used a stripe shape, and first, the black stripes were formed and then each of the fluorescent substances was applied to the gaps between the stripes to form the fluorescent film 108. A material mainly composed of graphite normally used was used as the material for the black stripes, but other conductive material having low light transmissivity and reflectivity may alternatively be used.

[0041]

A precipitation or printing technique is used for

1104-01-00

applying fluorescent substances on the glass substrate 107. In this embodiment of color display, a slurry method was used. In color display, the similar coat film is obtained using a printing method. A metal back 109 is usually arranged on the inner surface of the fluorescent film 108. The metal back 109 is provided in order to enhance the luminance of the display panel by causing the rays of light emitted from the fluorescent substance(s) and directed to the inside of the enclosure to be fully reflected toward the face plate 110, to use it as an electrode for applying an accelerating voltage to electron beams and to protect the fluorescent substance against damages that may be caused when negative ions generated inside the enclosure collide with it. The metal back is prepared by smoothing the inner surface of the fluorescent film (in an operation normally referred to as "filming") and forming an Al film thereon by vacuum vapor deposition in a manufacturing step subsequent to the preparation of the fluorescent film.

[0042]

A transparent electrode (not shown) may be formed on the face plate 110 facing the outer surface of the fluorescent film 108 in order to raise the electroconductivity of the fluorescent film. In this embodiment, the transparent electrode was omitted because a sufficient electroconductivity was obtained by only the metal back.

# IN 04-01-00

Care should be taken to accurately align each set of pieces of fluorescent substances of the primary colors and a corresponding electron-emitting device, if a color display is involved, before the above listed components of the enclosure are bonded together.

[0043]

The prepared glass container was then evacuated by means of an exhaust pipe (not shown) and an exhaust pump to achieve a sufficient degree of cacuum inside the container. Thereafter, the electroconductive film of each of the electron-emitting devices arranged on the substrate was subjected to an electric forming operation, where a voltage was applied to the device electrodes of the electron-emitting devices by way of the external terminals Dox1 through Doxm and Doyl through Doyn to produce electron-emitting devices 104 having each of an electron-emitting region formed in the electroconductive film. The enclosure was hermetically sealed by heat melting the exhaust pipe at a degree of vacuum of about  $10^{-6}$  Torr. Finally, a getter treatment was conducted in order to maintain the degree of vacuum after the sealing.

The enclosure may be subjected to a getter operation just before or after the sealing the enclosure. The getter operation is a treatment to form a vapor deposited film by heating a getter (not shown) arranged at a given

1104-01-00

position inside of the image display apparatus by resistance heating or high frequency heating. A getter normally contains Ba as a principal ingredient and the formed vapor deposited film can maintain the degree of vacuum of the inside of the enclosure by its adsorption effect.

[0044]

The finished image forming apparatus was operated by applying a voltage to each electron-emitting device by way of the external terminals Dox1 through Doxm and Doyl through Doyn to cause the electron-emitting devices to emit electrons. Meanwhile, a high voltage of greater than several kV was applied to the metal back 109 or a transparent electrode (not shown) by way of a high voltage terminal Hv to accelerate electron beams and cause them to collide with the fluorescent film 108, which by turn was energized to emit light to display intended images.

[0045]

The constitution mentioned above gives an outline for manufacturing the image forming apparatus, and for example, details such as materials for each members are not limited to the above described materials. An arrangement configuration of a plurality of electron-emitting devices 104 on the substrate 101 may be a configuration in which a plurality of device rows, each

# III. 04-01-00

of device rows comprising a plurality of electron-emitting devices connected to a pair of wiring electrodes, are arranged. In this case, a control electrode (usually referred to as grid) for selecting the device for emitting the fluorescent substance is arranged in the direction perpendicular to the device rows. Thus, the constitution of an image forming apparatus is properly selected so as to be suitable for its application.

[0046]

## [Embodiments]

The present invention will be described specifically by giving examples.

[0047]

### Example 1

In this example, a complex of a metal salt of an organic acid and a near infrared ray absorbing coloring matter having an amino group was used as the near infrared ray absorbing compound. As a typical example, an example using a complex of palladium acetate (Compound No. 37a) and an anthraquinone derivative (Compound No. 29) is described. Fig. 3 is process steps illustrating one example of a method for manufacturing an electron-emitting device of the present invention. An electron-emitting device was manufactured on basis of Fig. 3.

[0048]

A pattern of photoresist (RD-2000N-41, available from

1104-01-00

Hitachi Chemical Co., Ltd.) having openings of a desired profile for a pair of device electrodes was formed on a quartz substrate as an insulating substrate 1 and then Ti of a thickness of 50 Å and Ni of a thickness of 1,000 Å were successively deposited on the substrate by vacuum vapor deposition. Thereafter, the Ni/Ti laminated film was lifter-off by dissolving the photoresist pattern with an organic solvent to form a pair of device electrodes 5 and 6 having a distance L1 between the device electrodes of 10  $\mu\text{m}$  and a width W1 of the device electrodes of 300  $\mu\text{m}$ .

[0049]

A solution of the above near infrared ray absorbing organic metal complex (0.5 % by weight) in dimethyl sulfoxide was rotationally applied on the substrate including the device electrodes 5 and 6 at 1,000 rpm. Thereafter, the region inside the dotted line in Fig. 4 was irradiated with laser beams from a semiconductor laser having a wavelength of 830 nm, an output of 30 mW, a pulse width of 3  $\mu\text{sec}$  and a beam diameter of 2  $\mu\text{m}$ , while shifting the substrate at a pitch of 0.5  $\mu\text{m}$ , thereby the entire region inside the dotted line in Fig. 4 was irradiated with the laser beams and baked. Thereafter, the near infrared ray absorbing organic metal compound in the unnecessary region was removed by washing with dimethyl sulfoxide and acetone.

1104-01-00

[0050]

A thin film 2 for forming an electron-emitting region composed of Pd as a principal element thus formed had a film thickness of 100  $\text{\AA}$  and a sheet resistance of  $5 \times 10^4 \Omega/\square$ . Thereafter, the thin film for forming an electron-emitting device was subjected to an electric forming by electrically energizing with a triangular wave having  $T_1$  of 10 microseconds,  $T_2$  of 100 microseconds and a wave height of 7V for 10 seconds to obtain an electron-emitting device. Subsequently, the electron emitting performance of the electron-emitting device was evaluated. As a result, the emission current of  $\mu\text{A}$  with the device voltage of 14V or an electron-emitting efficiency of 0.07 % was observed, showing a good electron emitting performance.

[0051]

Example 2

A pair of device electrodes 5 and 6 were formed on a quartz substrate in the same manner as in Example 1. A solution of a near infrared ray absorbing organic metal composition comprising an organic metal compound (nickel acetylacetonate, Compound No. 38b, 1 % by weight) and a polymethine coloring matter (Compound No. 8, 1 % by weight) in butyl acetate was rotationally applied to the substrate including the device electrodes at 1,000 rpm.

1104-01-00

[0052]

Thereafter, the region inside the dotted line in Fig. 4 was irradiated with laser beams from a semiconductor laser having a wavelength of 830 nm, an output of 30 mW, a pulse width of 3  $\mu$ sec and a beam diameter of 2  $\mu$ m, while shifting the substrate at a pitch of 0.5  $\mu$ m, thereby the entire region inside the dotted line in Fig. 4 was irradiated with the laser beams and baked. Thereafter, the near infrared ray absorbing organic metal composition in the unnecessary region was removed by washing butyl acetate and acetone.

[0053]

Thereafter, the thin film for forming an electron-emitting region obtained was subjected to an electric forming in the same manner as in Example 1 to prepare an electron-emitting device. Subsequently, the electron emitting performance of the electron-emitting device was evaluated. As a result, the emission current of 0.8  $\mu$ A with the device voltage of 14V or an electron-emitting efficiency of 0.1 % was observed, showing a good electron emitting performance.

[0054]

Example 3

A pair of device electrode 5 and 6 were formed on a quartz substrate in the same manner as in Example 1. A suspension of a near infrared ray absorbing organic

1104-01-00

metal substance (a zinc phthalocyanine derivative, Compound No. 2a, 2 % by weight) in poly(vinyl alcohol) was applied to the substrate including the device electrodes.

[0055]

Thereafter, the region inside the dotted line in Fig. 4 was irradiated with laser beams from a semiconductor laser having a wavelength of 830 nm, an output of 30 mW, a pulse width of 3  $\mu$ sec and a beam diameter of 2  $\mu$ m at 10 pulses per one portion, while shifting the substrate at a pitch of 0.5  $\mu$ m, thereby the entire region inside the dotted line in Fig. 4 was irradiated with the laser beams and baked. Thereafter, the poly(vinyl alcohol) and the near infrared ray absorbing organic metal composition in the unnecessary region were removed by washing with alcohol and water.

[0056]

Thereafter, the thin film for forming an electron-emitting region obtained was subjected to an electric forming in the same manner as in Example 1 to prepare an electron-emitting device. Subsequently, the electron emitting performance of the electron-emitting device was evaluated. As a result, the emission current of 1.2  $\mu$ A with the device voltage of 14V or an electron-emitting efficiency of 0.11 % was observed, showing a good electron emitting performance.

[0057]

1104-01-00

Example 4

An image display apparatus was manufactured using the electron-emitting devices prepared by the method of Example 1 according to a method for manufacturing an image display apparatus mentioned above.

An thin film 2 for forming an electron-emitting region was formed on a substrate in the same manner as in Example 1.

An image display apparatus as shown in Fig. 8 was manufactured using this substrate according to the method mentioned above. The number of the electron-emitting devices was 100 x 100 pixels.

[0058]

After the enclosure was evacuated to a sufficient degree of vacuum, an electric forming was conducted by applying a voltage to the assembly through external terminals Dxl through Dxm and Dyl through Dyn to form electron-emitting devices, thereby manufacturing an image forming apparatus.

[0059]

The obtained image forming apparatus could display images by applying an voltage to the devices through external terminals Dxl through Dxm and Dyl through Dyn, to cause electrons emit, while applying a high voltage to a metal back through a high voltage terminal Hv.

[0060]

1104-01-00

Comparative Example 1

A pair of device electrodes 5 and 6 were formed on a quartz substrate in the same manner as in Example 1. A solution of an organic metal compound (palladium acetate, 1 % by weight) in butyl acetate was rotationally applied to the substrate at 1,000 rpm. Thereafter, the region inside the dotted line in Fig. 4 was irradiated with laser beams from a semiconductor laser having a wavelength of 830 nm, an output of 30 mW, a pulse width 3  $\mu$ sec and a beam diameter of 2  $\mu$ m, while shifting the substrate at a pitch of 0.5  $\mu$ m, thereby the entire region inside the dotted line in Fig. 4 was irradiated with the laser beams and baked. Thereafter, the organic metal compound in the unnecessary region was removed by washing with butyl acetate. A thin film mainly composed of Pd thus prepared had a film thickness of less than the measuring limit (20  $\text{\AA}$ ).

[0061]

[Effect of the Invention]

According to the present invention, as described above, a thin film comprising an organic metal compound is easily baked using laser beams by imparting a near infrared ray absorbing property to the thin film comprising an organic metal compound, and the process steps are simplified and the electrode material is not subjected to an excessive thermal load and also the organic metal compound is

1104-01-00

efficiently utilized by simultaneously conducting baking and patterning the thin film.

[Brief Description of the Drawings]

[Fig. 1]

Fig. 1 is process steps of a method for manufacturing an electron-emitting device according to the present invention.

[Fig. 2]

Fig. 2 is a drawing illustrating an electron-emitting device manufactured by the method according to the present invention.

[Fig. 3]

Fig. 3 is a drawing illustrating one example of a method for manufacturing an electron-emitting device according to the present invention.

[Fig. 4]

Fig. 4 is a drawing showing a region to be irradiated with laser beams in Example 1.

[Fig. 5]

Fig. 5 is a drawing illustrating a gauging system for determining the performance of an electron-emitting device according to the present invention.

[Fig. 6]

Fig. 6 is a graph illustrating a voltage waveform that is applied to an electric forming step.

[Fig. 7]

1104-01-00

Fig. 7 shows voltage-current relationships of an electron-emitting device according to the present invention.

[Fig. 8]

Fig. 8 is a drawing illustrating a method for manufacturing an image forming apparatus such as a display apparatus using a method for manufacturing according to the present invention.

[Fig. 9]

Fig. 9 is a drawing illustrating patterns of a fluorescent film used in an image forming apparatus.

[Fig. 10]

Fig. 10 is a schematic view illustrating a typical device constitution of the conventional surface conduction electron-emitting device.

[Description of Reference Numerals or Symbols]

1: insulating substrate

2: thin film for forming electron-emitting region

3: electron-emitting region

4: thin film including electron-emitting region

5, 6: device electrode

8: thin film comprising near infrared ray absorbing organic metal substance

10: metal or metal oxide film particle film

R: region to be irradiated by semiconductor laser

30, 32: ammeter

1104-01-00

31: power source  
33: high voltage power source  
34: anode  
101: substrate  
102: rear plate  
103: support frame  
104: electron-emitting device  
105: X-directional wiring  
106: Y-directional wiring  
107: glass substrate  
108: fluorescent film  
109: metal back  
110: face plate  
111: enclosure

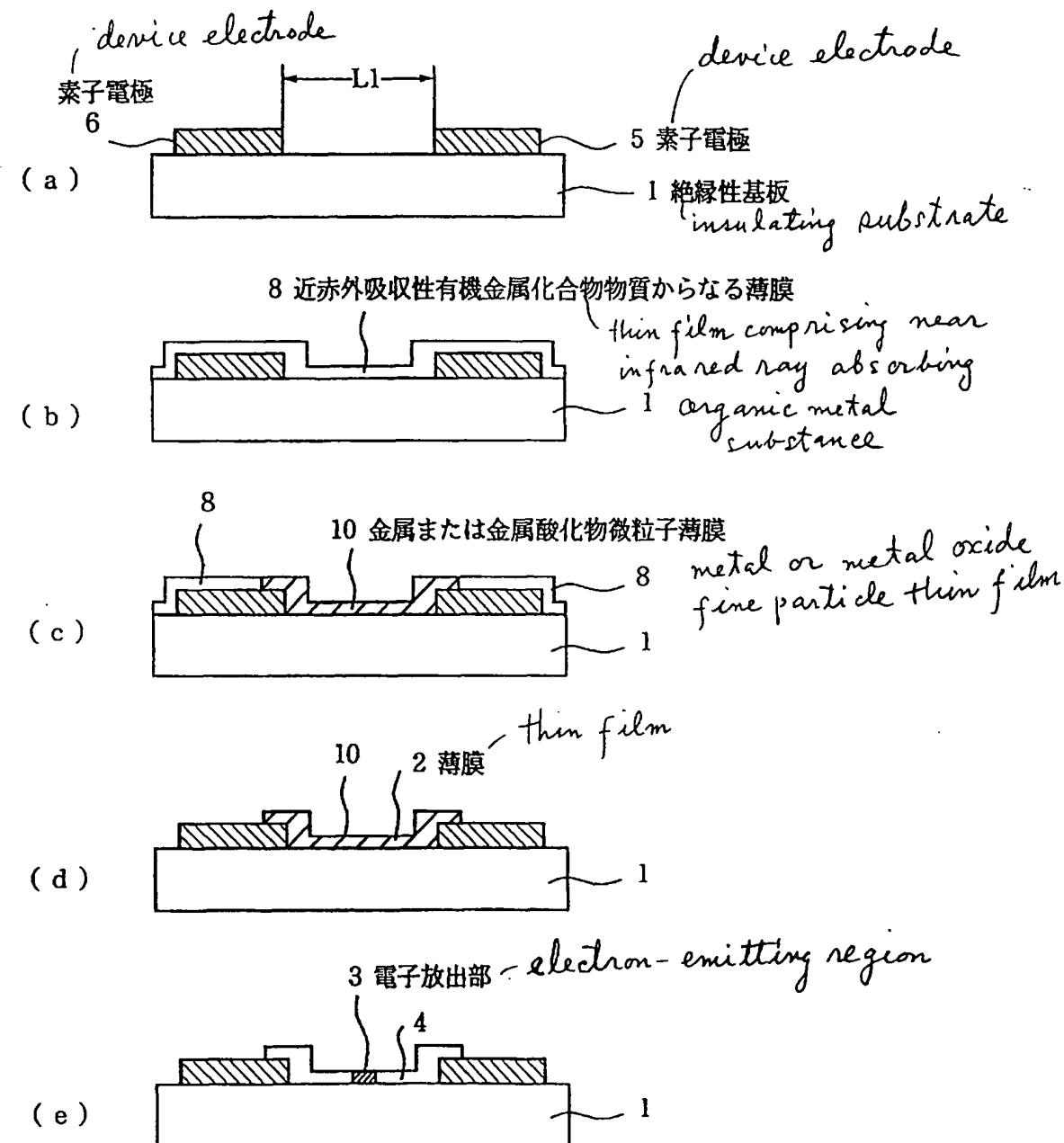
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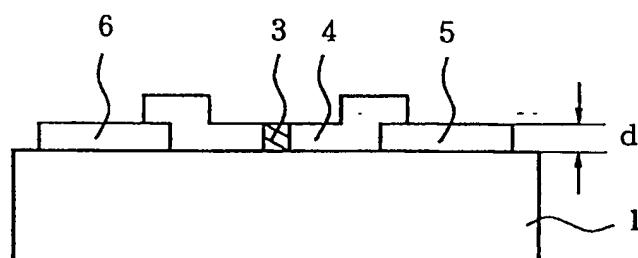
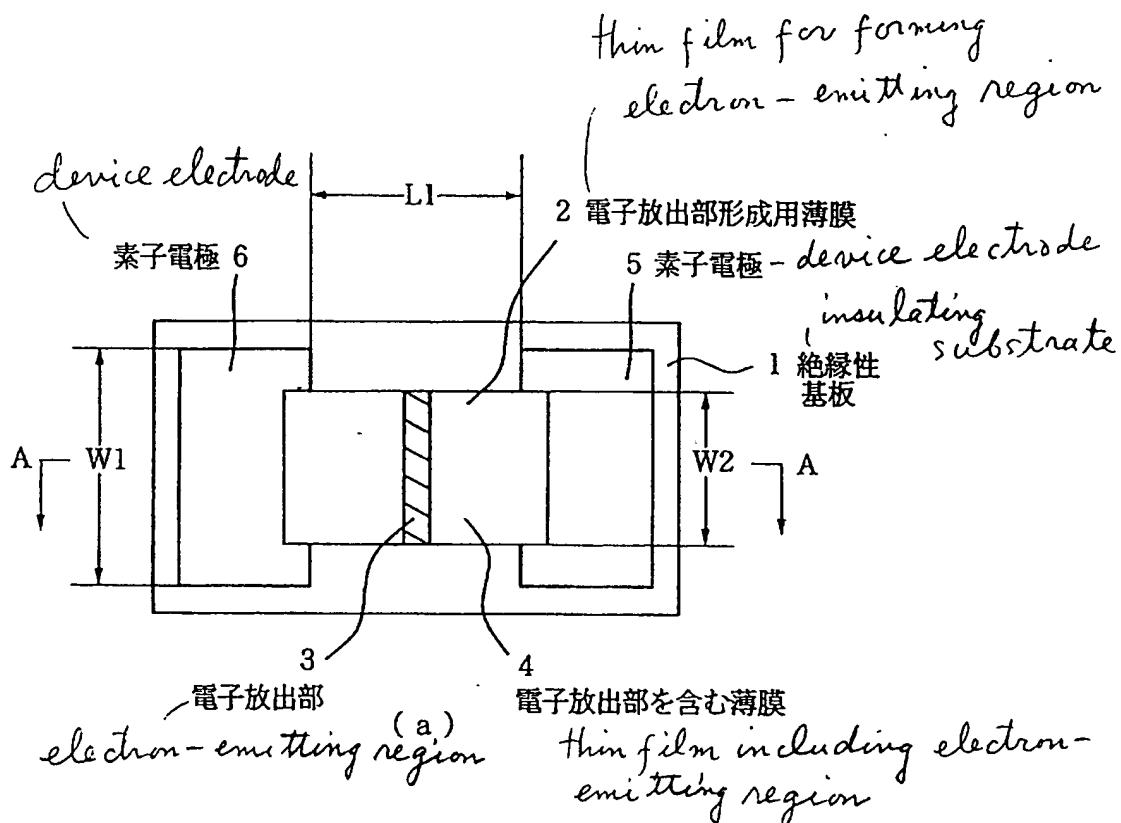
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図面 Drawings

【図1】 Fig. 1

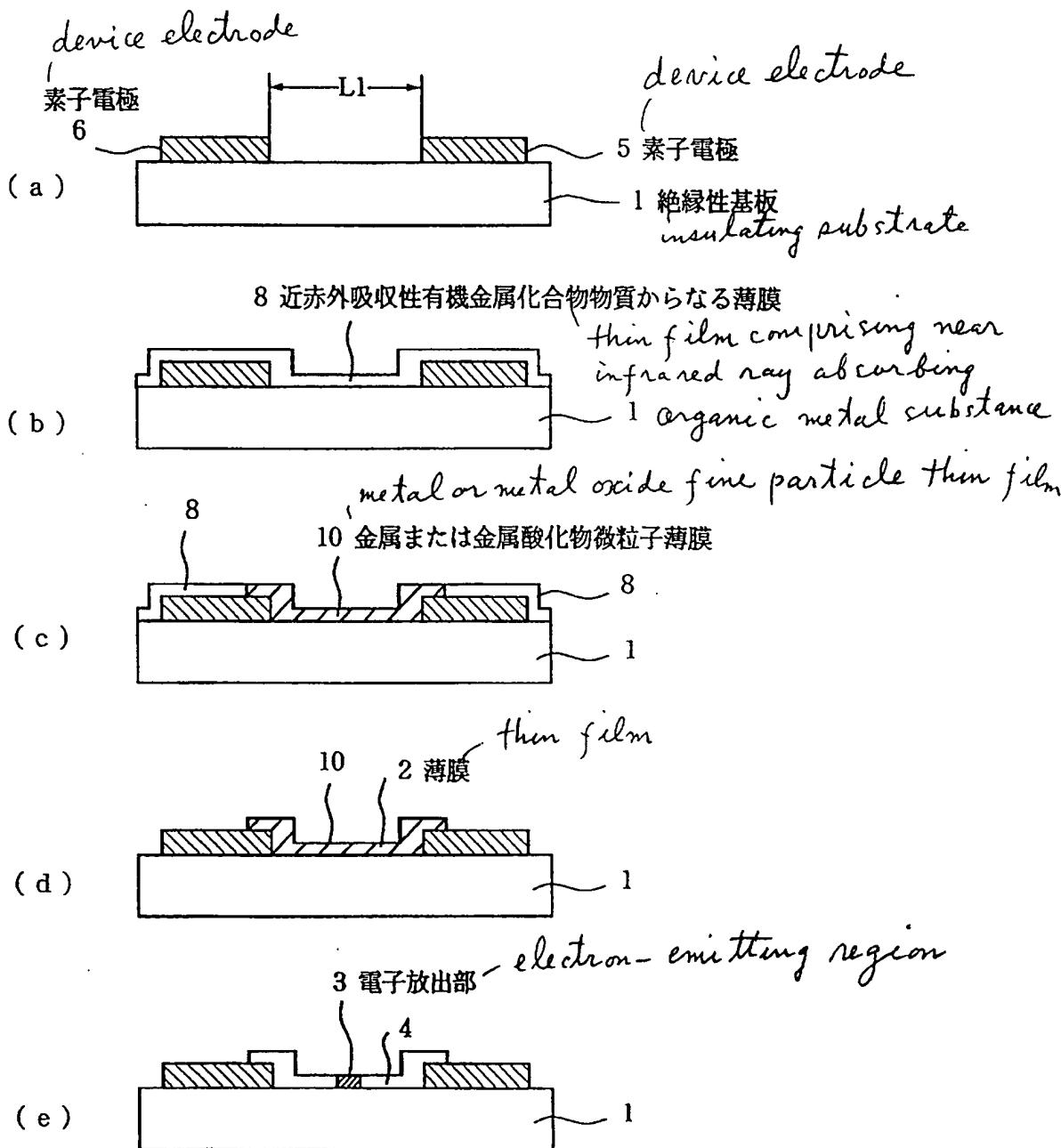


【図2】 Fig. 2

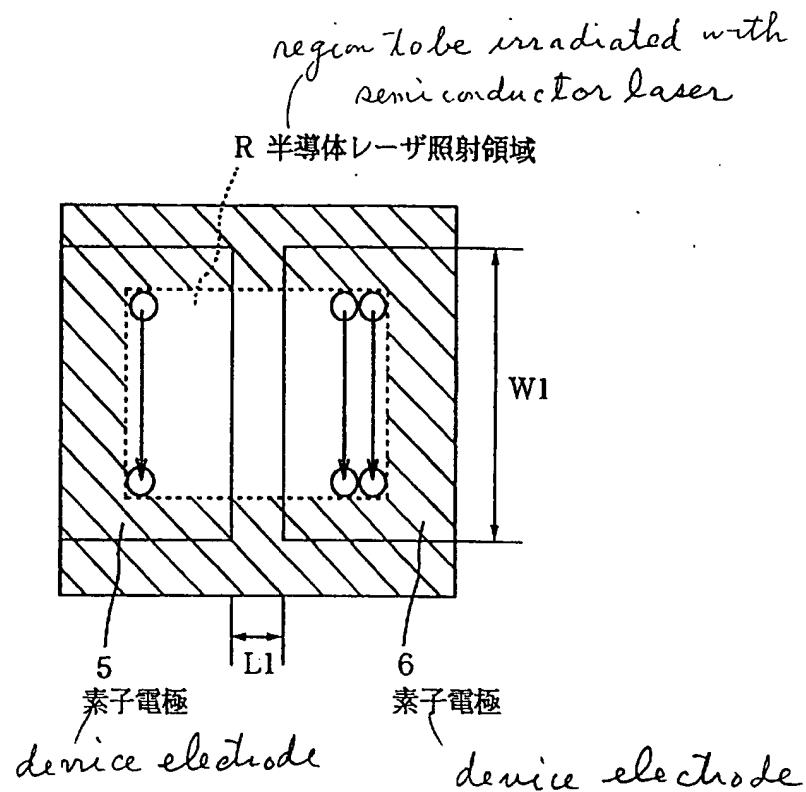


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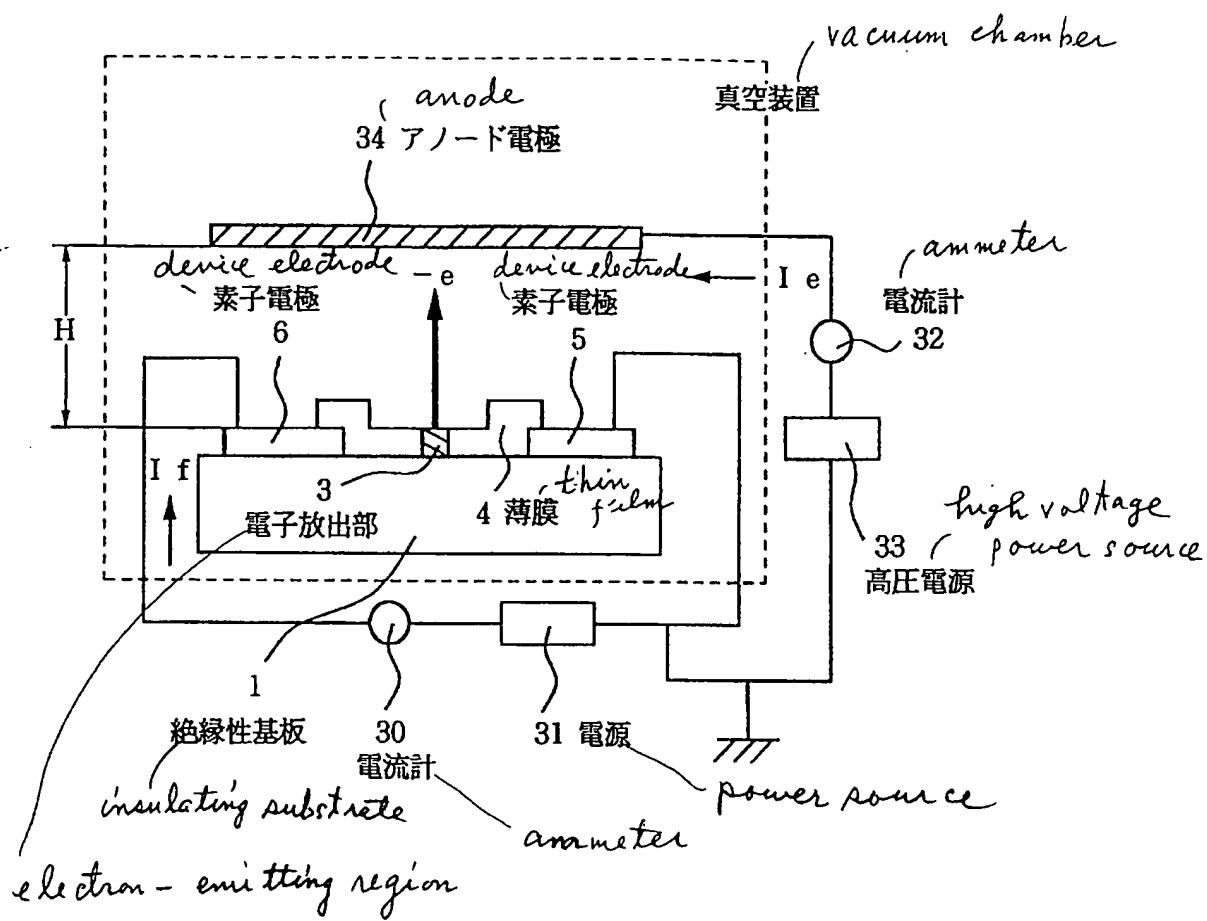
【図3】 Fig. 3



【図4】 Fig. 4



【図5】 Fig.5

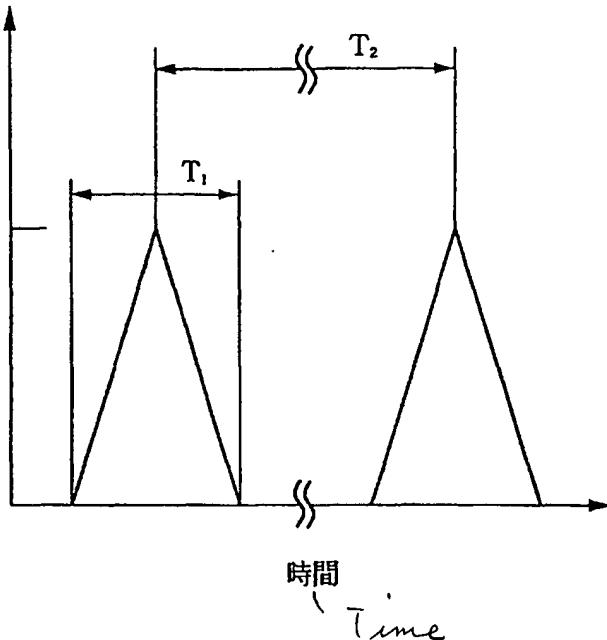


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【図6】 Fig. 6

Forming voltage (Peak value)

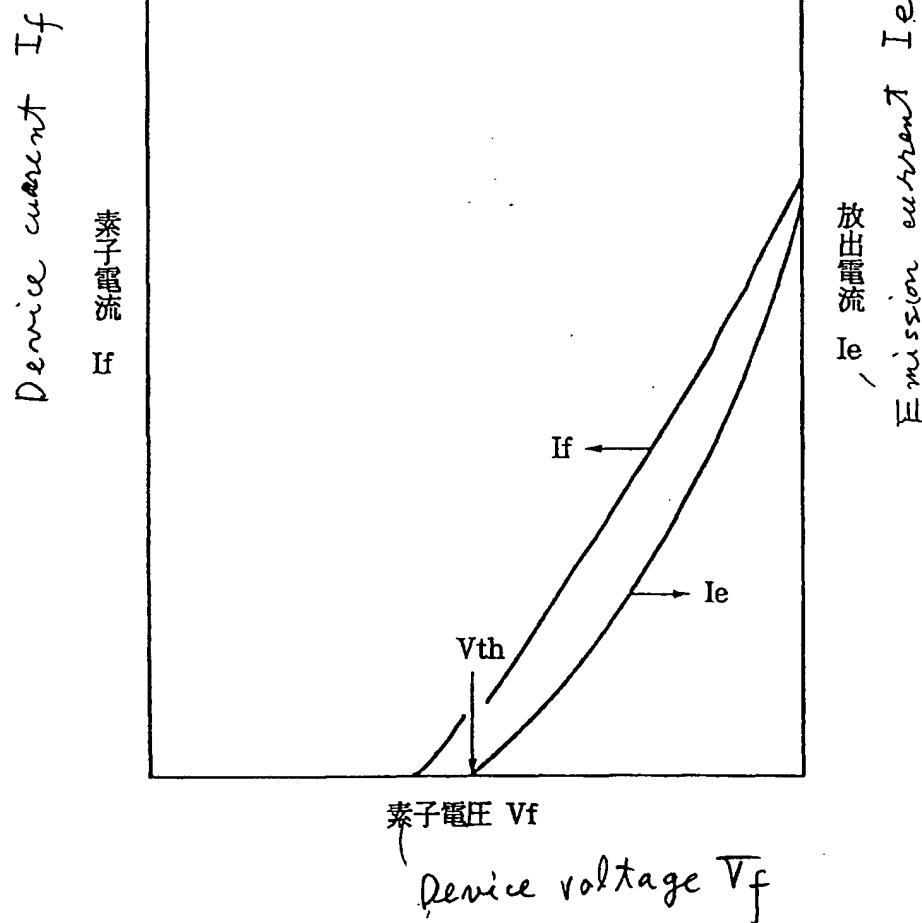
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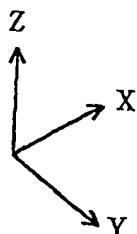
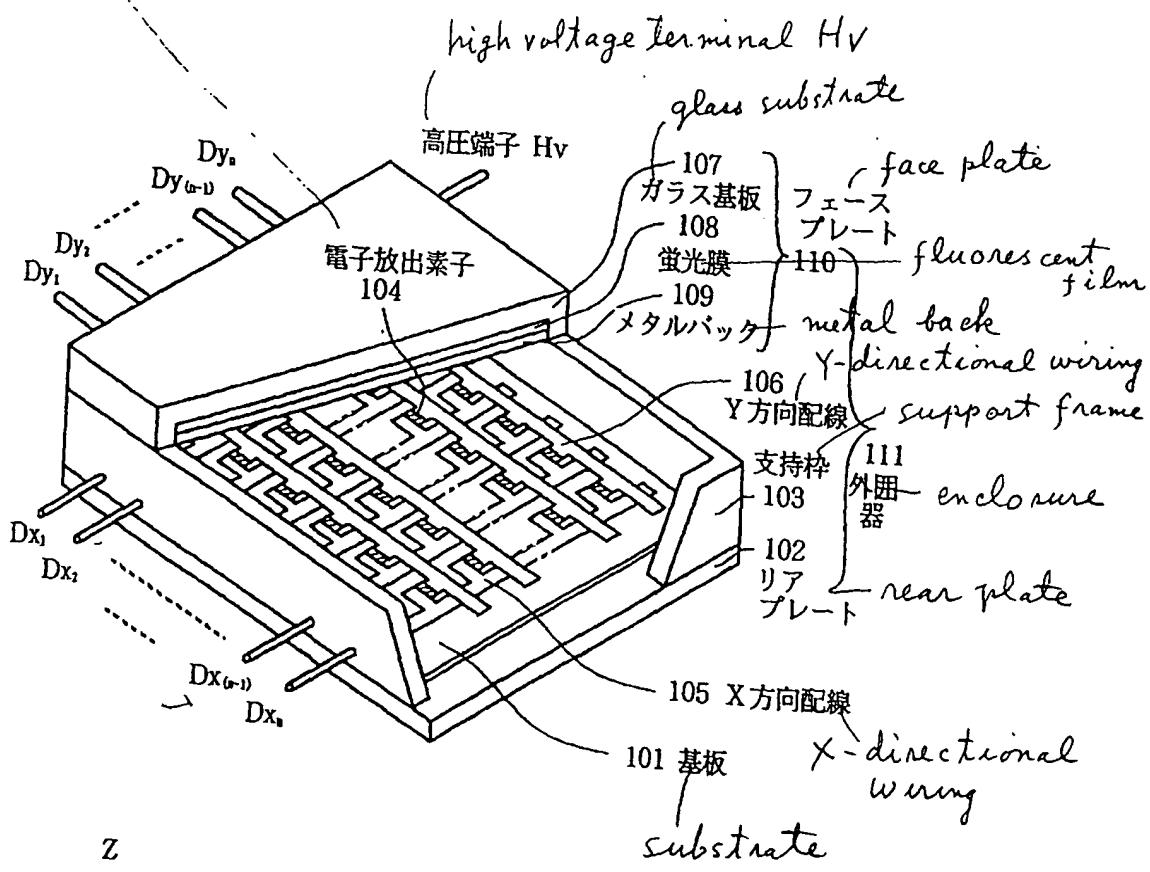
【図7】 Fig. 7



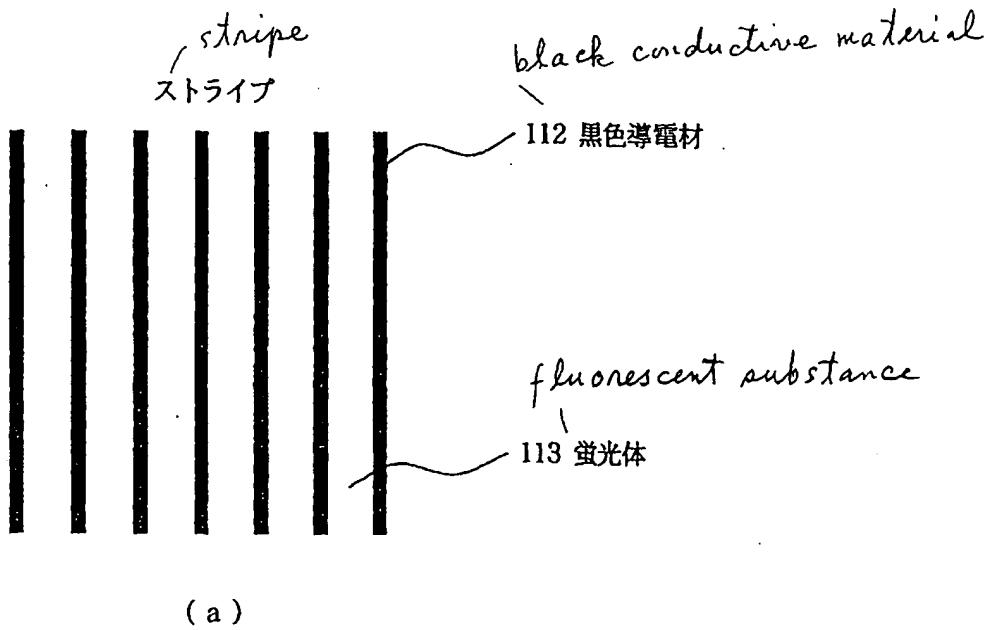
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【図8】 Fig.8

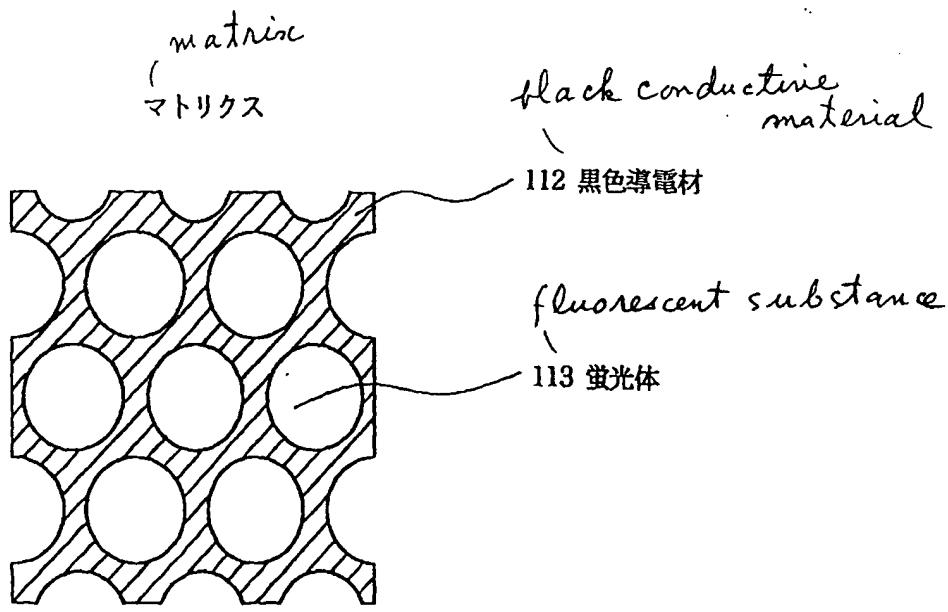
electron-emitting device



【図9】 Fig.9



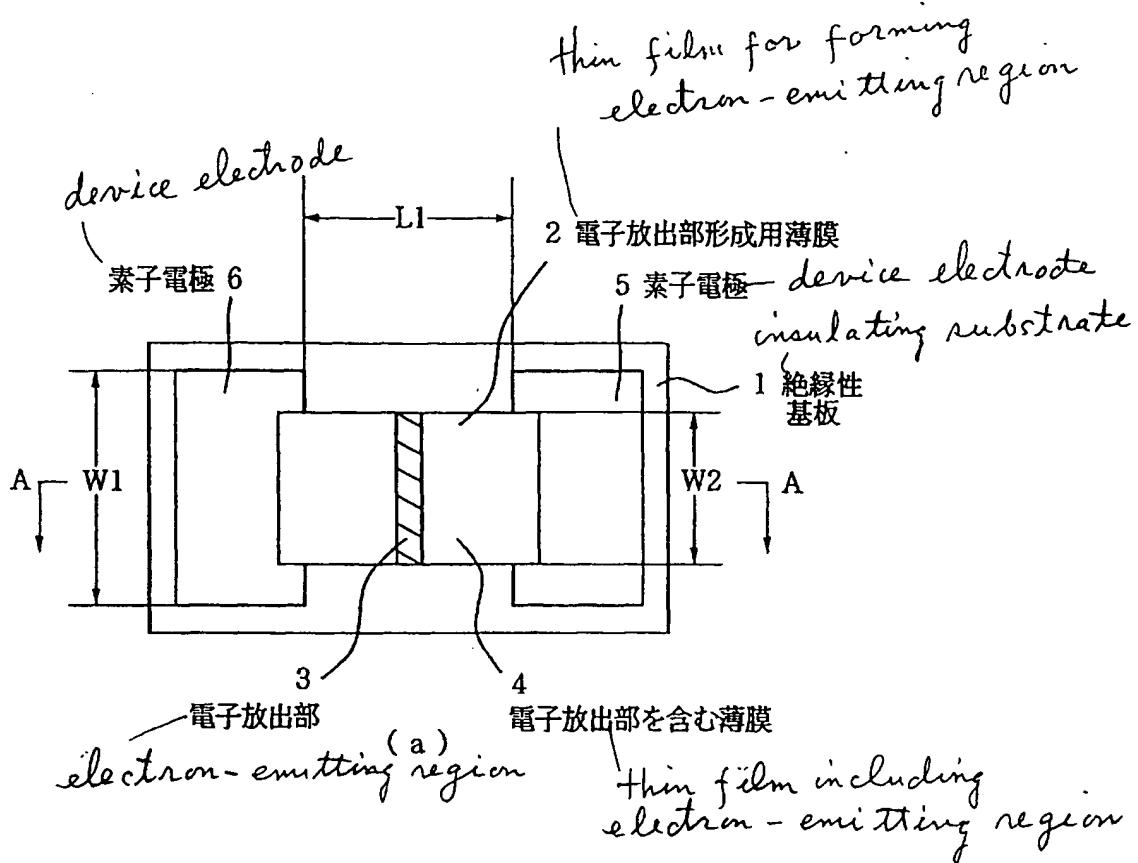
(a)



(b)

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【図10】 Fig. 10



(b)